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Supplementary Material Available: Tables S1-S4, listing crystal data and details of data collection, fractional atomic coordinates and isotropic thermal parameters, anisotropic thermal displacement parameters, and least-squares plane equations for $[CuL(H_2O)]_n$ (5 pages); a listing of calculated and observed structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Oxamidato Complexes. 2. Copper(II) and Nickel(II) Complexes with Oxamide-*N*,*N'*-diacetic Acid: Solution Study, Synthesis, Crystal Structures, and Magnetic Properties

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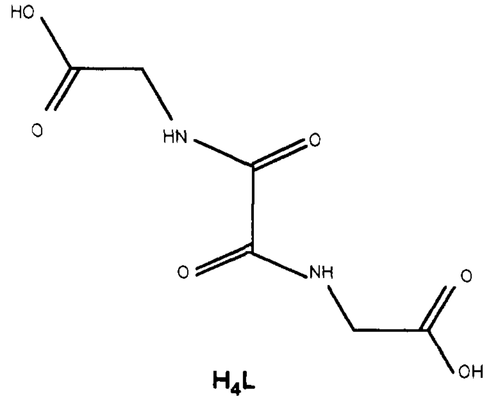
The complex formation between Cu(II) and Ni(II) and oxamide-*N*,*N'*-diacetic acid (H_4glyox, H_4L) has been studied by potentiometry in aqueous solution at 25 °C in 0.1 mol dm^{-3} $NaNO_3$. The two first acidity constants of H_4L were $pK_{a1} = 2.86$ (1) and $pK_{a2} = 3.64$ (1). The logarithms of the equilibrium constants for its Cu(II) and Ni(II) complexes according to the equations $M^{2+} + H_2L^{2-} \leftrightarrow M(H_2L)$ and $2M^{2+} + H_2L^{2-} \leftrightarrow M_2L + 2H^+$ were 2.62 (1) and −2.18 (1) for Cu(II) and 1.93 (1) and −11.09 (1) for Ni(II), respectively. Two new compounds of formulas $\{[Cu(H_2glyox)(H_2O)_3]\cdot 4H_2O\}_n$ (**1**) and $[Ni_2(glyox)(H_2O)_6]\cdot 4H_2O$ (**2**) have been synthesized, and their crystal structures have been determined by X-ray crystallographic methods. The compounds crystallize in the monoclinic system, space groups $P2_1/m$ and $P2_1/c$, respectively, with cell dimensions $a = 6.0070$ (4) Å, $b = 22.329$ (1) Å, $c = 5.8015$ (3) Å, $\beta = 105.784$ (5)°, and $Z = 2$ for **1** and $a = 6.9885$ (7) Å, $b = 9.0530$ (6) Å, $c = 14.250$ (1) Å, $\beta = 99.655$ (7)°, and $Z = 2$ for **2**. The structure of **1** was solved by direct methods and that of **2** by the heavy-atom method. Least-squares refinements converged at $R = 0.026$ in both cases. The structure of **1** consists of infinite chains in which the oxamidato ligand, deprotonated only at the carboxylate groups, is bis-monodentate. The copper atom is situated at a mirror plane in a distorted square-pyramidal environment. The copper–copper intrachain separation is 13.321 Å. The structure of **2** consists of neutral binuclear units in which the oxamidato ligand is fully deprotonated and acts in a bis-tridentate fashion. Nickel coordination is distorted octahedral. The nickel–nickel intramolecular separation is 5.368 Å. The magnetic properties of **1** and **2** have been investigated in the 4.2–300 K temperature range. A Curie law is observed for **1**, whereas a relatively strong antiferromagnetic coupling is observed for **2**, evidenced by a rounded maximum in the susceptibility curve at ~41 K ($J = -25$ cm^{-1} and $g = 2.25$, where J is the exchange parameter in the isotropic Hamiltonian $\hat{H} = -J\hat{S}_A\cdot\hat{S}_B$). These magnetic behaviors are easily understood in the frame of a localized-orbital model of exchange interactions. We discuss the striking influence of acid–base properties upon the coordination ability of the ligand and the very different physical properties which can result therefrom.

Introduction

N-Substituted and N,N'-disubstituted oxamides such as I have played a key role in the design of polymetallic systems. The versatility of these ligands, which is based on (i) the wide variety of substituted derivatives which can be realized, yielding different numbers of chelate rings with different donor atoms, (ii) their easy cis–trans conformational change affording symmetric and asymmetric oxamidato bridges, and (iii) the bidentate character of the mononuclear metal–oxamidato complex,[2-4] allows the formation of di,[2c,4a,b,5-8] tri-,[9] and tetranuclear[10] complexes as well as bi-



H$_4$L

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metallic chains.[8d,9c,11] The mononuclear copper(II) complexes have been used as chelating bricks to synthesize polymetallic systems exhibiting predictable magnetic properties[4b] and irregular spin-state structures[12] and very recently to build the exciting molecular-based ferromagnets.[8d,11] A recent review of the copper(II) complexes with N,N'-substituted oxamides and related ligands summarizes the coordination chemistry of such ligands.[13] Square-planar diamagnetic species are obtained in the case of oxamidate-containing nickel(II) complexes due to the coordination of the strong-field amide N atoms. This fact explains the lack of magnetic studies concerning these complexes in contrast to the relevant magnetochemical role played by the corresponding copper(II) compounds. However, paramagnetic nickel(II)–oxamide complexes can be obtained if the strength of the ligand field of the substituted oxamide is decreased. This can be achieved by choosing judiciously the nature of the donor group, X (carboxylate instead of amine nitrogen or pyridine for instance) and introducing angular strain (series of five-membered chelate rings instead of alternating six- and five-membered ones) as shown in this paper.

Studies dealing with the formation of oxamidato complexes in solution are scarce,[14] while considerable efforts have been devoted to the study of such species in the solid state and more especially in the field of molecular materials. As a part of our research on the complexes of oxamide derivatives with first-row transition-metal ions,[15] we have investigated the formation of Cu(II) and Ni(II) complexes with oxamide-*N*,*N'*-diacetic acid, H_4glyox (hereafter noted H_4L), both in aqueous solution and in the solid state. We report here on the complexing ability of L^{4-} with regard to H^+, Cu(II), and Ni(II). The crystal structures of the complexes $\{[Cu(H_2glyox)(H_2O)_3]\cdot 4H_2O\}_n$ (**1**) and $[Ni_2(glyox)(H_2O)_6]\cdot 4H_2O$ (**2**) together with their magnetic properties are also presented.

Experimental Section

Materials. All chemicals were of reagent grade and were used without further purification. Carbonate-free NaOH (0.1 mol dm^{-3}) and HNO_3 (0.1 mol dm^{-3}) were used in the potentiometric titrations. All potentiometric measurements were carried out using 0.1 mol dm^{-3} $NaNO_3$ as background electrolyte.

Ligand and Complex Preparations. The ligand oxamide-*N*,*N'*-diacetic acid was synthesized by following the general procedure reported in ref 13. A 20-mmol amount of glycine dissolved in about 25 mL of water was neutralized with equivalent NaOH, and 10 mmol of diethyl oxalate in 25 mL of ethanol was added to the aqueous solution. After the mixture was heated at 60 °C with stirring, an excess of HCl (pH ~1) was added for precipitation of white crystals of free H_4L. The product was filtered off, washed with cold water, ethanol, and ether, and air-dried. Anal. Calcd for $C_6H_8N_2O_6$: C, 35.30; H, 3.95; N, 13.72. Found: C, 35.20; H, 4.07; N, 13.85.

Light turquoise-colored plates of complex **1** suitable for X-ray analysis were obtained from aqueous solutions of copper(II) nitrate trihydrate and H_4L in a 1:1 molar ratio at pH ~3 by slow evaporation. The crystals were collected, washed with cold water, and air-dried. They gave a satisfactory analysis for $\{[Cu(H_2glyox)(H_2O)_3]\cdot 4H_2O\}_n$ (**1**). Anal. Calcd for $C_6H_{20}N_2O_{13}Cu$ (**1**): C, 18.39; H, 5.15; N, 7.15. Found: C, 18.56; H, 5.50; N, 7.30.

Slightly wedge-shaped green crystals of complex **2** suitable for X-ray analysis were obtained by a procedure analogous to the one described for **1** but at pH ~6.5. The crystals gave a satisfactory analysis for $[Ni_2(glyox)(H_2O)_6]\cdot 4H_2O$ (**2**). Anal. Calcd for $C_6H_{24}N_2O_{16}Ni_2$ (**2**): C, 14.48; H, 4.86; N, 5.63. Found: C, 14.65; H, 5.02; N, 5.70.

Table I. Crystallographic Data for $\{[Cu(H_2L)(H_2O)_3]\cdot 4H_2O\}_n$ (**1**) and $[Ni_2L(H_2O)_6]\cdot 4H_2O$ (**2**)

	1	**2**
chem formula	$C_6H_{20}N_2CuO_{13}$	$C_6H_{24}N_2Ni_2O_{16}$
a, Å	6.0070 (4)	6.9885 (7)
b, Å	22.329 (1)	9.0530 (6)
c, Å	5.8015 (3)	14.250 (1)
β, deg	105.784 (5)	99.655 (7)
V, $Å^3$	748.8 (2)	888.8 (2)
Z	2	2
fw	391.77	497.68
space group	$P2_1/m$ (No. 11)	$P2_1/c$ (No. 14)
T, °C	21	21
λ, Å	0.71073	0.71073
ρ_{calcd}, g·cm^{-3}	1.737	1.860
μ, cm^{-1}	15.265	22.078
transm coeff	0.55–0.66	0.42–0.60
R^a	0.026	0.026
$R_w{}^b$	0.040	0.034
s^c	2.23	1.63

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$; the weighting scheme is defined by $w = 1/\sigma_F^2$ with $\sigma_F = \sigma_I(ILp)^{-1/2}$ and $\sigma_I = [\sigma_c^2 + (0.03N_{net})^2]^{1/2}$. ^{c} $s = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

Physical Techniques. IR spectra were taken on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets, and the reflectance spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer as Nujol mulls on filter paper.

Magnetic measurements were carried out on polycrystalline samples in the 4.2–300 K temperature range by means of a Faraday type magnetometer equipped with a helium flow cryostat. The magnetic field independence of the susceptibility was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Corrections for the diamagnetism were estimated from Pascal's constants as -192×10^{-6} and -238×10^{-6} cm^3 mol^{-1} for complexes **1** and **2**, respectively.

Potentiometric titrations were carried out by using a previously described titration assembly.[15] The temperature of all solutions was held at 25 °C by circulating constant-temperature water through the water-jacketed titration cell. The standard potential of the cell, $E°$, was calculated by applying the Gran method.[16] The computer program SUPERQUAD[17] was used to process data and calculate both basicity and stability constants. Solutions of H_4L with $c_L = 10^{-3}$–10^{-2} mol dm^{-3} and of metal to ligand ratios in the range 0.5–3 with $c_M = (2–5) \times 10^{-3}$ mol dm^{-3} were titrated with NaOH (0.1 mol dm^{-3}) to determine the acidity constants and complex formation, respectively.

Crystallographic Data Collection and Structure Determination. All measurements were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal data are summarized in Table I. A full length table of crystallographic data is given as supplementary material (Table S1). The crystals used for data collection were 0.60 × 0.28 × 0.41 and 0.49 × 0.20 × 0.19 mm for **1** and **2**, respectively. Cell dimensions were in each case determined from 25 reflections with 2θ angles in the range 13–25°. In each case, reflections in the octants $h,k,\pm l$ up to $2\theta = 60°$ were collected; 2233 and 2576 unique reflections were measured for **1** and **2**, respectively. Three reference reflections monitored throughout each data collection showed no significant sign of crystal deterioration. The random error in any one reflection is calculated as $\sigma_I = [\sigma_c^2 + (0.03\sigma_c^2)^2]^{1/2}$. The data were corrected for absorption by a Gaussian integration method, the ranges of transmission factors being 0.55–0.66 and 0.42–0.60 (μ = 15.265 and 22.078 cm^{-1}) for **1** and **2**, respectively.

For compound **1** the intensity data distribution did not conclusively distinguish space groups $P2_1$ and $P2_1/m$. The structure was solved in the noncentrosymmetric space group by direct methods. The full-matrix least-squares refinement in $P2_1$ led to unreasonable differences between chemically equivalent bonds and angles and to large correlation coefficients between parameters. Refinement was hence continued in the centrosymmetric space group. A disordered model for one of the water

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Table II. Atomic Parameters[a,b]

atom	*x/a*	*y/b*	*z/c*	B_{eq}, Å^2
		(a) $\{[Cu(H_2L)(H_2O)_3]\cdot 4H_2O\}_n$ (**1**)		
Cu	0.41466 (3)	0.25000	0.14609 (3)	1.529 (4)
O1	0.4121 (1)	0.33709 (5)	0.1360 (2)	2.14 (2)
O2	0.0954 (2)	0.33490 (5)	0.2638 (2)	2.75 (2)
O3	0.2931 (2)	0.48660 (5)	0.6331 (2)	2.51 (2)
O4	0.7565 (2)	0.2500	0.0680 (3)	2.60 (3)
O5	0.5374 (3)	0.2500	0.5017 (3)	2.94 (3)
O6	0.2203 (3)	0.2500	−0.1926 (3)	2.47 (3)
O7	0.3376 (2)	−0.08960 (6)	0.1257 (2)	3.16 (2)
O81	0.1066 (3)	0.6670 (1)	0.3565 (3)	2.78 (4)
O82	0.0094 (4)	0.6437 (1)	0.3189 (4)	3.07 (4)
N1	0.0668 (2)	0.45853 (5)	0.2664 (2)	1.89 (2)
C1	0.2469 (2)	0.36223 (5)	0.1997 (2)	1.71 (2)
C2	0.2477 (2)	0.42979 (6)	0.1860 (2)	1.96 (2)
C3	0.1069 (2)	0.48468 (5)	0.4789 (2)	1.64 (2)
H1	−0.066 (3)	0.4602 (9)	0.191 (3)	0.5 (3)*
H4	0.849 (4)	0.2135 (9)	0.113 (4)	2.0 (5)*
H5	0.633 (6)	0.280 (2)	0.554 (7)	9 (1)*
H6	0.146 (3)	0.2206 (9)	−0.229 (4)	1.7 (4)*
H21	0.383 (3)	0.446 (1)	0.278 (4)	1.9 (4)*
H22	0.216 (3)	0.441 (1)	0.022 (3)	1.5 (4)*
H71	0.402 (4)	−0.106 (1)	0.044 (4)	2.5 (5)*
H72	0.421 (3)	−0.072 (1)	0.202 (4)	1.7 (4)*
		(b) $[Ni_2L(H_2O)_6]\cdot 4H_2O$ (**2**)		
Ni	0.38541 (3)	0.18522 (2)	0.35433 (1)	1.707 (3)
O1	0.5184 (2)	0.3920 (1)	0.35264 (8)	2.11 (2)
O2	0.7330 (2)	0.5416 (1)	0.43666 (8)	2.82 (2)
O3	0.6881 (2)	0.0230 (1)	0.60010 (8)	2.19 (2)
O4	0.2155 (2)	0.1807 (2)	0.22588 (9)	3.75 (3)
O5	0.1512 (2)	0.2805 (2)	0.40985 (9)	2.77 (2)
O6	0.60033 (2)	0.0850 (1)	0.28734 (8)	2.59 (2)
O7	0.8683 (2)	0.2975 (2)	0.2474 (1)	3.41 (3)
O8	0.8909 (3)	−0.0584 (3)	0.4111 (2)	6.34 (5)
N1	0.5590 (2)	0.1811 (1)	0.47838 (9)	1.84 (2)
C1	0.6427 (2)	0.4227 (2)	0.4257 (1)	1.81 (3)
C2	0.6832 (2)	0.3075 (2)	0.5046 (1)	1.97 (3)
C3	0.5724 (2)	0.0585 (2)	0.5238 (1)	1.68 (2)
H21	0.818 (3)	0.283 (2)	0.517 (1)	0.5 (4)*
H22	0.666 (3)	0.352 (2)	0.566 (1)	0.5 (4)*
H41	0.233 (3)	0.150 (2)	0.186 (1)	0.7 (4)*
H42	0.129 (3)	0.211 (2)	0.223 (1)	1.0 (4)*
H51	0.182 (3)	0.344 (3)	0.450 (2)	1.9 (5)*
H52	0.128 (5)	0.326 (3)	0.385 (2)	5.1 (9)*
H61	0.567 (3)	0.029 (2)	0.242 (1)	0.7 (4)*
H62	0.670 (4)	0.047 (3)	0.324 (2)	3.1 (6)*
H71	0.779 (4)	0.236 (4)	0.262 (2)	4.2 (7)*
H72	0.823 (4)	0.348 (3)	0.215 (2)	2.0 (5)*
H81	1.043 (6)	−0.026 (5)	0.389 (2)	9 (1)*
H82	0.95 (1)	−0.089 (6)	0.483 (5)	19 (2)*

[a] Estimated standard deviations in the last significant digits, as obtained from the least-squares refinement, are given in parentheses. [b] *B* values marked with an asterisk denote isotropically refined atoms. The isotropic equivalent thermal parameter is given as $B_{eq} = 4/3\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Bond Distances (Å) and Angles (deg) Involving Non-Hydrogen Atoms

(a) $\{[Cu(H_2L)(H_2O)_3]\cdot 4H_2O\}_n$ (**1**)[a]			
Bond Distances			
Cu–O1	1.9454 (7)	O3–C3	1.228 (1)
Cu–O4	2.220 (1)	N1–C2	1.444 (1)
Cu–O5	1.993 (1)	N1–C3	1.326 (1)
Cu–O6	1.994 (1)	C1–C2	1.511 (1)
O1–C1	1.278 (1)	C3–C3^{i}	1.533 (2)
O2–C1	1.234 (1)		
Bond Angles			
O1–Cu–O1^{ii}	176.70 (4)	C2–N1–C3	122.26 (8)
O1–Cu–O4	89.67 (2)	O1–C1–O2	124.31 (8)
O1–Cu–O5	91.65 (2)	O1–C1–C2	114.19 (7)
O1–Cu–O6	88.44 (2)	O2–C1–C2	121.49 (8)
O4–Cu–O5	96.26 (5)	N1–C2–C1	114.44 (7)
O4–Cu–O6	97.18 (4)	O3–C3–N1	126.29 (8)
O5–Cu–O6	166.56 (5)	O3–C3–C3^{i}	120.3 (1)
Cu–O1–C1	115.51 (6)	N1–C3–C3^{i}	113.42 (9)
(b) $[Ni_2L(H_2O)_6]\cdot 4H_2O$ (**2**)[b]			
Bond Distances			
Ni–O1	2.0921 (9)	O2–C1	1.244 (2)
Ni–O3^{i}	2.0858 (9)	O3–C3	1.282 (1)
Ni–O4	2.008 (1)	N1–C2	1.447 (2)
Ni–O5	2.117 (1)	N1–C3	1.280 (2)
Ni–O6	2.131 (1)	C1–C2	1.525 (2)
Ni–N1	1.969 (1)	C3–C3^{i}	1.541 (2)
O1–C1	1.270 (2)		
Bond Angles			
O1–Ni–O3^{i}	160.97 (3)	O6–Ni–N1	90.87 (5)
O1–Ni–O4	101.74 (5)	Ni–O1–C1	115.51 (8)
O1–Ni–O5	90.71 (5)	Ni–O3^{i}–C3	109.72 (8)
O1–Ni–O6	91.37 (4)	Ni–N1–C2	117.99 (8)
O1–Ni–N1	79.59 (4)	Ni–N1–C3	116.87 (8)
O3^{i}–Ni–O4	97.28 (5)	C2–N1–C3	124.4 (1)
O3^{i}–Ni–O5	90.33 (5)	O1–C1–O2	123.7 (1)
O3^{i}–Ni–O6	89.21 (4)	O1–C1–C2	118.1 (1)
O3^{i}–Ni–N1	81.38 (4)	O2–C1–C2	118.1 (1)
O4–Ni–O5	88.45 (6)	N1–C2–C1	108.7 (1)
O4–Ni–O6	86.60 (5)	O3–C3–N1	128.9 (1)
O4–Ni–N1	177.16 (5)	O3–C3–C3^{i}	118.3 (1)
O5–Ni–O6	174.93 (5)	N1–C3–C3^{i}	112.7 (1)
O5–Ni–N1	94.05 (5)		

[a] Roman numeral superscripts refer to the following equivalent positions relative to *x*, *y*, *z*: (i) −*x*, 1 − *y*, 1 − *z*; (ii) *x*, $^1/_2$ − *y*, *z*. [b] Roman numeral superscript refers to the following equivalent position relative to *x*, *y*, *z*: (i) 1 − *x*, − *y*, 1 − *z*.

molecules (O81/O82) had to be adopted.

For compound **2** the Ni position was determined from a Patterson map, and the remaining non-hydrogen atoms were localized in subsequent Fourier maps.

In both cases, non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized in difference Fourier maps (except those of disordered water O81/O82) and refined isotropically. Extinction parameters were included and adjusted in the final refinement cycles ($g = 2.28 \times 10^{-6}$ and 3.68×10^{-7}, respectively). The refinements, based on 2101 and 2228 reflections with $F_o > 2\sigma$, converged at $R = 0.026$, $R_w = 0.040$, $s = 2.23$ and $R = 0.026$, $R_w = 0.034$, $s = 1.63$ for compounds **1** and **2**, respectively. Scattering factors, including corrections for anomalous dispersion, and programs used are those of refs 18 and 19. All calculations were done on a MICRO-VAX II computer. Atomic parameters for the two structures are listed in Table II. Anisotropic thermal parameters and structure factors are given as supplementary material (Tables S2a, S2b, S6a, and S6b).

Results and Discussion

Description of the Structures. For complexes **1** and **2**, the structural building blocks are shown in Figure 1 and selected bond distances and angles are listed in Table III. Distances and angles involving hydrogen atoms are found in the supplementary material (Tables S3a and S3b).

Structure of 1. The structure of this complex consists of $[Cu(H_2L)]_n$ chains running along the 2_1 axis, Cu being situated at a crystallographic mirror plane and the midpoint of the oxamide C–C bond at an inversion center. The ligand is deprotonated only at the terminal carboxylate groups and is bis-monodentate. The Cu coordination is approximately square pyramidal with two water molecules (O5 and O6) and two symmetry-related carboxylato oxygen atoms (O1 and O1^{ii}) in the equatorial plane and a water molecule (O4) in the axial position. The sixth position is screened by the proximity of the carboxylato oxygen O2 (Cu–O2 = 2.907 Å). Atomic deviations from a least-squares plane through O1, O1^{ii}, O5, and O6 are 0.123, 0.123, −0.119, and −0.126 Å, with Cu displaced 0.111 Å from this plane. The dihedral angle between this equatorial plane and the plane of the carboxylate group (O1, O2, C1) is 97.0°. The oxamido group (O3, N1, C3, O3^{i}, N1^{i}, C3^{i}) is planar within experimental error and makes an angle of

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(18) Cromer, D. T.; Waber, T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99 (Table 2.2 B).

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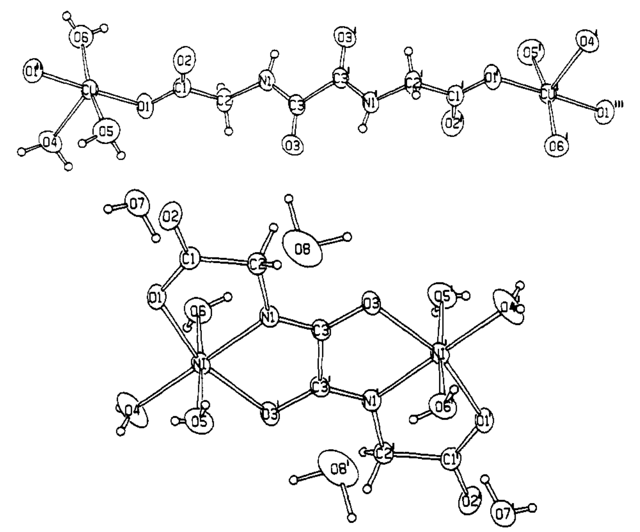

Figure 1. (a) Top: Section of the chain in complex **1** with the atom-numbering scheme used. Waters of crystallization O7 and O81/O82 have been omitted for clarity. Thermal ellipsoids are plotted at the 70% probability level. Hydrogen atoms are given an arbitrary radius. Symmetry operations: (i) $-x, 1 - y, -z$; (ii) $x, {}^1/_2 - y, z$; (iii) $-x, {}^1/_2 + y, -z$. (b) Bottom: Binuclear unit in complex **2** with the atom-numbering scheme used. Thermal ellipsoids are plotted at the 70% probability level. Hydrogen atoms are given in arbitrary radius. Symmetry operation: (i) $1 - x, -y, 1 - z$.

76.1° with the carboxylate group. Torsional angles are listed in Table S5a.

The copper–copper separation within the chain is 13.321 Å. The closest *inter*chain separations are those associated with the unit cell translations along *c* (5.802 Å) and *a* (6.007 Å). The chains are interconnected through an extensive hydrogen bond network. The alternative positions of the disordered water molecule (O81, O82) are both suitable for hydrogen bonding to O2, O6, and O7, while only O81 forms a hydrogen bond to O5. A list of hydrogen bonds is included in Table S4a.

Structure of 2. This compound forms centrosymmetric binuclear molecules with L^{4-} acting as a bis-terdentate ligand. Ni has a distorted slightly elongated octahedral environment with three atoms from the L^{4-} ligand and one water molecule in the equatorial plane and two water molecules filling the axial positions. The equatorially coordinated atoms lie within ±0.024 Å from the best least-squares plane through these atoms, the Ni atom being situated only 0.023 Å from the plane. The oxamido group (N1, O3, C3, N1^i, O3^i, C3^i) is planar within experimental error, Ni deviating by 0.228 Å from this plane. The dihedral angle between the planes of the equatorial ligands and the oxamido group is 9.6°. Torsional angles are listed in Table S5b. The deprotonation at N1 and the metal coordination at O3 and N1 lead to highly significant changes in bond distances N1–C3 and O3–C3 as compared to the corresponding distances in complex **1**: 1.326 (1) and 1.228 (1) Å for **1** and 1.280 (2) and 1.282 (1) Å for **2**. N1–C3 and O3–C3 distances in **1** are very close to the reported ones for neutral and substituted oxamides.[20] When the oxamide is deprotonated and both oxygen and nitrogen atoms are coordinated to metal ions, a more effective π-delocalization in the NCO fragment results, as evidenced by the nearly identical N1–C3 and O3–C3 distances in the deprotonated coordinated amide. These structural features have already been observed by some of us in a recently reported oxamide-containing copper(II) complex[15] and are the reason for the noticeable efficiency of the oxamidato bridge to transmit electronic effects (see magnetic properties).

The nickel-nickel separation within each binuclear unit is 5.368 Å. The shortest intermolecular metal–metal distances occur between molecules related by a screw-axis translation, nickel–nickel $(1 - x, {}^1/_2 + y, {}^1/_2 - z) = 5.787$ Å, and by a unit cell translation along *a*, nickel–nickel $(1 + x, y, z) = 6.989$ Å. All oxygen atoms participate in hydrogen bonds; a list is found in Table S4b.

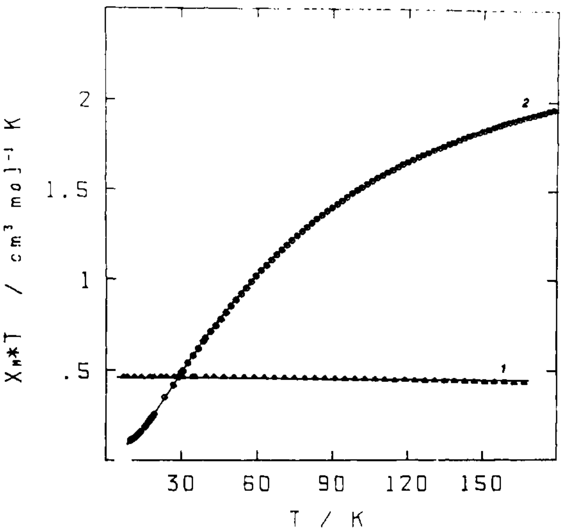

Figure 2. Thermal variation of the molar susceptibility for complexes **1** and **2** in the form $\chi_M T$ versus T: (open points) experimental results; (solid line) best theoretical fit.

Electronic and IR Spectra. The reflectance spectrum of **1** consists of a charge-transfer band centered at 28 600 cm^{-1} and a broad band at 13 500 cm^{-1}, which contains the unresolved d–d transitions. The position of this last band is consistent with a square-pyramidal structure as observed. The square-planar surrounding and coordination of strong-field amine N atoms can be ruled out because d–d transitions at much higher energy would be observed in such a case.[13] The reflectance spectrum of **2** is typical of an octahedral Ni(II) complex,[21] exhibiting three maxima at 8930, 14 400, and 29 400 cm^{-1} (Δ_0 = 8930 cm^{-1}; nephelauxetic ratio β = 0.858). A shoulder is observed on the middle band at 15 260 cm^{-1}. This splitting is due to spin–orbit coupling that mixes the $^3T_{1g}(F)$ and ^1E_g states, which are very close in energy for Δ_0 values of ~9000 cm^{-1}.[22]

The IR spectra of **1** and **2** display a band (s, br) centered at 3400 cm^{-1}, which reveals the presence of water in both cases. In addition, a single absorption of medium intensity is observed at 3340 cm^{-1} (ν(N–H) stretching band) for **1**, revealing the existence of N–H amide groups. This band has been observed for free H_4L ligand at 3320 cm^{-1}. The amide I band is located at 1640 (s) and 1580 (s) cm^{-1} for complexes **1** and **2**, respectively. Taking into account that this absorption is centered at 1640 (s) cm^{-1} for free H_4L, it can be inferred that a protonated amide group is present in complex **1**, as shown recently by some of us in a related oxamide-containing Cu(II) complex.[15] As far as complex **2** is concerned, the shift to lower wavenumbers of the amide I band is consistent with the presence of a bridging oxamidato ligand. ν_a(COO) and ν_{as}(COO) stretching vibrations of carboxylate groups appear as strong absorptions at 1670 and 1390 cm^{-1} for **1** and at 1660 and 1400 cm^{-1} for **2**, leading to Δ values [$\Delta = \nu_a$(COO) $- \nu_{as}$(COO)] of 280 (**1**) and 260 (**2**) cm^{-1}. These values are consistent with unidentate carboxylate coordination[23] in both cases. Moreover, Δ increases in the order Ni(II) < Cu(II), as expected for the increasing order of the metal–oxygen interaction.[24] All these spectral features are in agreement with the above described structures.

Magnetic Properties. The thermal variations of the molar susceptibility of both complexes are shown in Figure 2 as the

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product $\chi_M T$ versus T. The $\chi_M T$ product for complex **1** follows a Curie law, revealing that no exchange interaction between Cu(II) ions is operative in the temperature range studied. The data fit the Curie expression

$$\chi_M = \frac{N\beta^2 g^2}{4kT} + N\alpha \qquad (1)$$

with $g = 2.10$ and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. $N\alpha$ is the temperature-independent paramagnetism, and N, β, and k have their usual meanings. As far as complex **2** is concerned, the $\chi_M T$ product has the value expected for two $S = 1$ states at room temperature. Upon cooling down, it decreases markedly tending to an $S = 0$ ground state at low temperatures. A rounded maximum in the susceptibility curve is observed at about 41 K. Such a behavior is characteristic of a relatively strong antiferromagnetic interaction between two single-ion triplet states. Taking into account that the intramolecular interaction in **2** can be interpreted by the isotropic spin Hamiltonian $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$, where J is the exchange parameter and $S_A = S_B = 1$ (local spins), χ_M may be expressed as[25]

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \frac{\exp(J/kT) + 5\exp(3J/kT)}{1 + 3\exp(J/kT) + 5\exp(3J/kT)} + N\alpha \qquad (2)$$

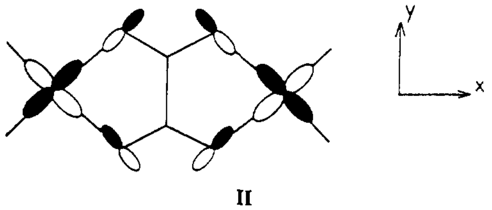
The last term in this expression is assumed to be 200×10^{-6} cm^3 mol^{-1} for two Ni(II) ions. We have not considered the effect of the zero-field splitting on the magnetic behavior because it is expected to be negligible due to the large stabilization of the singlet ground state.[26] A least-squares fit of all experimental data leads to $J = -25$ cm^{-1} and $g = 2.25$, with an agreement factor $R = \sum(\chi_{\text{exptl}}(i) - \chi_{\text{calcd}}(i))^2/\sum(\chi_{\text{exptl}}(i))^2$ of 1.25×10^{-4}.

The unpaired electron of the Cu(II) ion in complex **1** can be described by a magnetic orbital of d_{xy} symmetry partially delocalized on the nearest-neighbor O1, O1^{ii}, O5, and O6 atoms (average Cu(II)–O distance is 1.97 Å). The presence of an axial oxygen (O4) at 2.22 Å leads to a small admixture of d_{z^2} in the magnetic orbital. However, the spin density is large on the four basal atoms and much smaller on the apical position. The absence of coupling between Cu(II) ions in **1** is easily understood by taking into account that no overlapping between two d_{xy} magnetic orbitals through the H_2L^{2-} bridging ligand (the intrachain copper–copper separation is 13.321 Å) is possible. Although the interchain copper–copper distances are much shorter (about 6 Å) due to extensive hydrogen bonding, any interchain pathway for exchange interaction is not available.

As far as we are aware, this is the first time that the structure and magnetic properties of a μ-oxamidato nickel(II) binuclear complex are reported. Recently, it has been demonstrated that the oxamidato bridge exhibits a remarkable efficiency to propagate an antiferromagnetic interaction between two copper(II) ions separated by more than 5 Å.[4c,8a,b,15,27] This strong interaction is due to the large σ in-plane overlap of the d_{xy} magnetic orbitals through the oxamidato bridge as illustrated in II. However, the J value for complex **2** (−25 cm^{-1}) is much smaller than the reported ones for the related μ-oxamidato copper(II) binuclear complexes (−480 to −585 cm^{-1}). To deal with comparable values, the number of unpaired electrons on each paramagnetic center (one for Cu(II) and two for Ni(II)) should be taken into account; hence, the $n^2|J|$ values should be compared:[28]

$$\begin{array}{cc} J_{\text{Cu-Cu}} & > \; 4J_{\text{Ni-Ni}} \\ 530\ \text{cm}^{-1} & 100\ \text{cm}^{-1} \end{array}$$

They illustrate once more the special ability of Cu(II) as compared to Ni(II) to yield antiferromagnetic interactions, everything being equal. Similar trends have been observed for bridging bis-bidentate ligands such as 2,2′-bipyrimidine[29] and oxalate.[30] Keeping in mind the d_{xy} exchange pathway, the larger J value in the case of Cu(II) can be attributed to a larger spin delocalization on the bridge: the energies of the $3d_{\text{Cu(II)}}$ orbitals are lower than those of Ni(II)[31] and the M(II)–N,O (oxamidato bridge) average distance for Cu(II) is shorter than the observed one for Ni(II) (1.96 and 2.03 Å, respectively). Furthermore, the presence of ferromagnetic contributions in the case of Ni(II), which are negligible for Cu(II), contributes to the lowering of the observed J value for **2**. However, these considerations do not explain easily the considerable difference between such J values. We think that the main factor in this case could be the larger deviation of Ni(II) from the best basal plane (0.228 Å) when compared to Cu(II) (about 0.1 Å).[15,27]



II

Table IV. Equilibrium Data[a,b] for Basicity and Formation of Cu(II) and Ni(II) Complexes with L^{4-} in Aqueous Solution (25 °C and 0.1 mol dm^{-3} NaNO$_3$)

eq no.	reacn	log β
i	$2H^+ + L^{4-} \leftrightarrow H_2L^{2-}$	24.2 (5)
ii	$H^+ + H_2L^{2-} \leftrightarrow H_3L^-$	3.64 (1)
iii	$2H^+ + H_2L^{2-} \leftrightarrow H_4L$	6.50 (1)
iv	$Cu^{2+} + H_2L^{2-} \leftrightarrow Cu(H_2L)$	2.62 (1)
v	$2Cu^{2+} + H_2L^{2-} \leftrightarrow Cu_2L + 2H^+$	−2.18 (1)
vi	$2Cu^{2+} + L^{4-} \leftrightarrow Cu_2L$	22.0 (5)
vii	$Ni^{2+} + H_2L^{2-} \leftrightarrow Ni(H_2L)$	1.93 (2)
viii	$2Ni^{2+} + H_2L^{2-} \leftrightarrow Ni_2L + 2H^+$	−11.09 (1)
ix	$2Ni^{2+} + L^{4-} \leftrightarrow Ni_2L$	13.1 (5)

[a] Values in parentheses are standard deviations in the last significant digit. [b] Equilibria vi and ix are obtained by combining eq i with eqs v and viii, respectively.

Let us compare now the magnitude of the J values observed for complex **2** and the related μ-oxalato complex $[Ni_2(cyclam)_2ox](NO_3)_2$[30] (−25 and −34 cm^{-1}, respectively), where cyclam is 1,4,8,11-tetraazacyclotetradecane. The opposite trend was expected according to extended Hückel calculations on oxalate and oxamidate ligands:[27] the less electronegative the atoms of the bridge are (the higher the energy of the molecular orbitals of the bridge), the larger the delocalization of spin density on the bridge and consequently the larger the antiferromagnetic coupling J. Distortions of the octahedral environment of the metal ion are the origin of such unexpected results. Both oxalato and oxamidato bridges are planar in both structures. However, the Ni(II) ion is only 0.027 Å out of the oxalate plane whereas it is 0.228 Å out of the oxamidate one. This structural difference leads to a lowering of the σ in-plane overlap of the d_{xy} magnetic orbitals through the oxamidato bridge with respect to the oxalato one and, consequently, to a smaller J value.

Solution Study. The observed proton association constants of L^{4-} together with the stability constants of its Cu(II) and Ni(II) complexes are reported in Table IV. The protonation equilibrium constants of the ligand show that it behaves as a relatively strong base in the two first protonation steps and that its basicity is much decreased in the last two protonation steps. This is consistent with the different basicities of the deprotonated amide N atoms and

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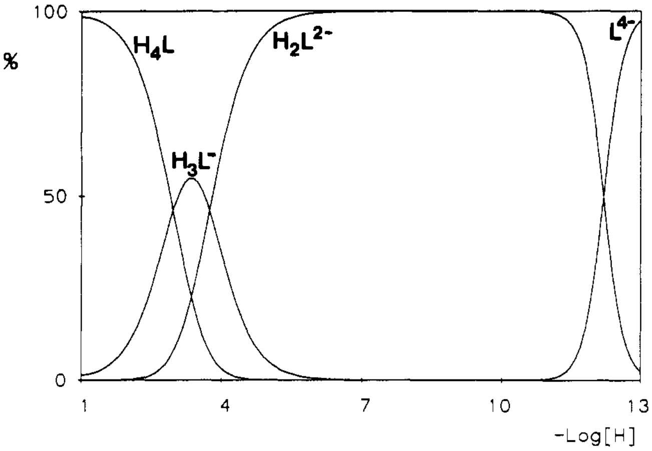

Figure 3. Distribution diagram for the system H^+–L^{4-}.

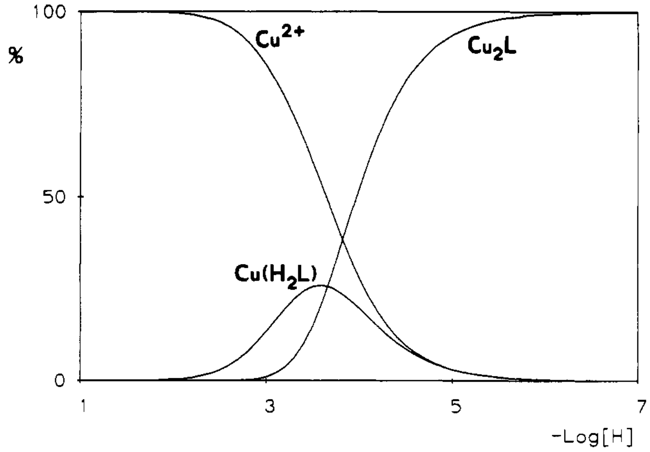

Figure 4. Distribution diagram for the system Cu^{2+}–L^{4-}–H^+ as a function of pH ($c_M = c_L = 5 \times 10^{-3}$ mol dm^{-3}).

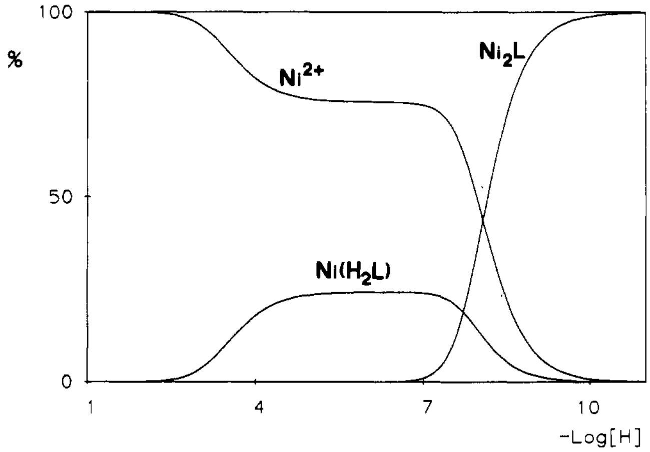

Figure 5. Distribution diagram for the system Ni^{2+}–L^{4-}–H^+ as a function of pH ($c_M = c_L = 5 \times 10^{-3}$ mol dm^{-3}).

carboxylate groups which are involved in such equilibria. The values for the logarithms of the stepwise protonation constants of the carboxylate groups of H_2L^{2-} are very close to the previously reported ones for such a ligand,[14a] and they are within the range observed for β-(electronegative group)-substituted carboxylic acids.[32] The distribution diagram for the system H^+/L^{4-} based on fitted equilibrium constants is depicted in Figure 3. The predominant species at lower pH values are H_4L and H_3L^- whereas the concentration of H_2L^{2-} becomes significant at pH > 3.40, being the only existing species in the range $5.60 \leq \text{pH} \leq 11.30$. At pH > 11.30, the deprotonation of the amide groups takes place to yield the L^{4-} species. The determination of the deprotonation constants involving N–H amide groups by potentiometry in aqueous solution is not reliable because very basic media are required. In fact, we have not observed any deprotonation of H_2L^{2-} for pH ≤ 11. This observation is general for some N,N′-disubstituted oxamides that we have studied. A detailed analysis of the potentiometric data in the range $11 \leq \text{pH} \leq 11.6$ reveals that some deprotonation occurs, the emf-computed data being consistent with the simultaneous loss of two protons ($\log \beta = 24.0$–24.6). In the present case, a value of 24.2 (5) (equilibrium i) was computed. The high value of its standard deviation reflects the low precision which is associated with the determination of this constant due to the low extent of deprotonation (ca. 10%) in a highly basic medium. The very weak acidity of the amides makes quantitative equilibrium measurements difficult, and a few values appear in the literature.[33] The acidity values observed for monoamides vary in the range $pK_a = 13$–15. Although no acidity constants were reported for oxamides, a greater acidity for them would not be unexpected due to the NCO π-delocalization in deprotonated oxamides, as well as to the major electron withdrawal of the other neighboring oxamide group. We have used the value of $\log \beta = 24.2$ (5) only to calculate the equilibrium constants of eqs vi and ix.

The complex-forming ability of H_4L with regard to M(II) (M = Ni, Cu) has been investigated in the 2.30–5 (M = Cu) and 2.50–9 (M = Ni) pH ranges. Potentiometric studies at greater pH values could not be carried out because of the precipitation of blue and green neutral binuclear M_2L complexes, respectively. Only the $M(H_2L)$ and M_2L species exist in the above mentioned pH ranges. The values of the stability constants for $M(H_2L)$ complexes (eqs iv and vii) are of the same order of magnitude as those for 1:1 M:carboxylate ligand complexes in which the carboxylate acts as a monodentate ligand.[32] Therefore, H_2L^{2-} most probably coordinates to Cu(II) and Ni(II) through one of its carboxylate groups to yield mononuclear $M(H_2L)$ species. The stability constant of the copper(II) complex (2.62 (1)) is somewhat greater than that of the corresponding nickel(II) complex (1.93 (2)), as expected according to the higher stability of the copper(II) complexes. As far as M_2L species are concerned, the high values of their logarithms of their stability constants (eqs vi and ix) reveal the chelating character of the L^{4-} ligand. In fact, the structure of complex **2** illustrates its bis-terdentate character. Again, the value of the stability constant for the Cu_2L species is greater than that for Ni_2L. It is interesting to note that the value of the stability constant for Cu_2L is somewhat smaller than the corresponding one for $[Cu_2(pmox)]^{2+}$ ($\log \beta = 26.1$ (1)),[15] where pmox is the dianion of *N,N′*-bis(2-pyridylmethyl)oxamide. Although in both cases five-membered chelate rings are involved, the higher affinity of copper(II) for pyridyl groups instead of carboxylate leads to such different values. The M(II)–H_4L system (M = Cu, Ni) was studied some years ago[14a] also by potentiometry in aqueous solution and only the $M(HL)^-$, Cu_2L, and $Ni(H_2L)$ species were found. The $M(HL)^-$ species was observed by us neither in the present study nor in other studies that we have carried out with related ligands such as H_2pmox[15] and H_2apox (*N,N′*-bis(3-aminopropyl)oxamide).[34] Moreover, the formation of Ni_2L and $Cu(H_2L)$ species, which are the parents of Cu_2L and $Ni(H_2L)$, respectively, was not observed in the early studies.[14a] However, in our study such species have been observed in solution and they have been isolated and characterized by X-ray diffraction (complexes **2** and **1**, respectively). It deserves to be pointed out that the $Cu(H_2L)$ complex exists as a mononuclear species in solution and it evolves slowly to complex **1** by polymerization at low pH values. The formation of other M^{2+}–L^{4-} complexes could not be followed because the precipitation of M_2L species occurs. Such species are, however, readily soluble in more basic media, yielding violet (Cu(II)) and yellow-green (Ni(II)) solutions of the ML^{2-}

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784 *Inorg. Chem.* **1992**, *31*, 784–791

mononuclear complexes that we have isolated as tetra- and pentahydrate sodium salts, respectively.

The synthesis of M_2L complexes was carried out in the light of the respective distribution diagrams based on fitted equilibrium constants (Figures 4 and 5). In order to obtain single crystals of such species, aqueous solutions of copper(II) nitrate (nickel(II) nitrate) and H_4L in a 2:1 molar ratio were prepared at pH = 3. In the case of copper(II), the slow polymerization of $Cu(H_2L)$ leads to the insoluble polymeric complex **1**. Nevertheless, $Cu_2L\cdot 6H_2O$ can be isolated as a powder in weakly acidic aqueous solutions. The nonpolymerization of the $Ni(H_2L)$ species allows in this case the formation of single crystals of the insoluble complex **2** in nearly neutral aqueous solutions.

Conclusions. The versatility of N,N′-disubstituted oxamides has allowed the synthesis of mono-, di-, and polynuclear complexes. Strong antiferromagnetic coupling is observed in the μ-oxamidato polynuclear compounds. This work shows how one must be careful when using the $n^2|J|$ values to estimate the magnitude of the exchange coupling in binuclear nickel(II) complexes from the known values for the corresponding copper(II) complexes through a given bridge. Although nickel(II)–oxamide complexes are usually diamagnetic, paramagnetic nickel(II) species can be obtained by tuning the strength of the ligand field using as tools appropriate N-substituted derivatives and angular strain. Finally, this report provides a new example of complementarity between solution and solid-state studies, showing how solution data can orientate the synthetic work in order to obtain the desired products.

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Registry No. **1**, 138490-13-8; **2**, 138490-14-9; H_4L, 23354-00-9; $Cu_2L(H_2O)_6$, 138490-15-0; $Ni(H_2L)(H_2O)_3$, 138516-45-7.

Supplementary Material Available: For **1** and **2**, stereoviews showing the crystal packing and listings of crystallographic data (Table S1), anisotropic thermal parameters (Tables S2a and S2b), bond distances and angles involving hydrogen atoms (Tables S3a and S3b), hydrogen-bonding data (Tables S4a and S4b), and torsional angles (Tables S5a and S5b) (11 pages); listings of calculated and observed structure factors (Tables S6a and S6b) (25 pages). Ordering information is given on any current masthead page.

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Oxamidato Complexes. 3. A Study of the Formation of Homo- and Heteropolymetallic Cu(II)–H_2apox–M(II) Complexes (H_2apox = *N*,*N*′-Bis(3-aminopropyl)oxamide; M(II) = Mn, Co, Ni, Cu, Zn, Cd). Synthesis and Crystal Structure of $[Cu_2(apox)(NCO)_2]$

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Potentiometric studies on the quaternary system Cu^{2+}–M^{2+}–$apox^{2-}$–H^+ (M = Mn, Co, Ni, Zn, Cd; $apox^{2-}$ = dianion of *N*,*N*′-bis(3-aminopropyl)oxamide, $C_8H_{18}N_4O_2$ (L^{2-})) have been carried out at 25 °C and 0.1 mol dm^{-3} $NaNO_3$. The proton association constants corresponding to the equilibria $L^{2-} + jH^+ \leftrightarrow H_jL^{(j-2)+}$ (β_j) were found to be log β_2 = 24.0 (2), log β_3 = 34.15 (2), and log β_4 = 43.60 (2). The values of the stability constants related to the equilibria $pCu^{2+} + qL^{2-} \leftrightarrow [Cu_pL_q]^{2(p-q)+}$ (β_{pq}) were log β_{11} = 20.33 (2), log β_{21} = 28.15 (2), log β_{32} = 51.68 (4), and log β_{43} = 74.35 (7), and those concerning the equilibria $pM^{2+} + qCu^{2+} + rL^{2-} \leftrightarrow [M_pCu_qL_r]^{2(p+p-r)+}$ (β_{pqr}) were log β_{111} = 23.86 (2) (Mn), 24.31 (2) (Co), 24.86 (2) (Ni), 24.87 (2) (Zn), and 23.80 (2) (Cd); log β_{122} = 46.79 (3) (Mn), 47.77 (3) (Co), 48.70 (4) (Ni), 48.81 (4) (Zn), and 46.90 (3) (Cd); and log β_{133} = 69.58 (3) (Mn), 70.66 (4) (Co), 72.30 (5) (Ni), 72.04 (5) (Zn), and 69.60 (3) (Cd). Since the ligand L^{2-} can exhibit both cis and trans conformations in its metal complexes, we have carried out an ab initio calculation to determine the energy involved in such conformational change using $(CH_3NCO)_2{}^{2-}$ as a model system. The trans conformation is predicted to lie 2.25 kcal below the cis one. Both the sign and magnitude of this result are in good agreement with our experimental data, and this result accounts for the anomalies observed in the values of the stepwise stability constants. The molecular structure of the complex $[Cu_2L(NCO)_2]$ has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with a = 13.237 (3) Å, b = 7.715 (3) Å, c = 7.161 (3) Å, β = 94.02 (1)°, and Z = 2. Refinement of the atomic parameters by least-squares techniques gave a final R factor of 0.036 (R_w = 0.039) for 1101 unique reflections having $I \geq 3\sigma(I)$. The structure consists of neutral one-dimensional chains of copper(II) ions bridged alternatively by the oxamidato and cyanato groups. The former acts as a bis-terdentate bridge whereas the latter is bound through nitrogen in an end-on fashion. The copper environment can be described as square pyramidal: the equatorial plane is defined by the oxygen and nitrogen atoms of the amide, the nitrogen atom of the amine group, and the nitrogen atom of the cyanato ligand whereas the apical position is filled by a nitrogen atom of another cyanato group. The values of the stability constants of the system Cu^{2+}–M^{2+}–L^{2-} are compared and discussed in light of the available structural data.

Introduction

For more than a decade, the design and synthesis of heteropolymetallic complexes have been a challenging field for inorganic chemists.[2] In general, the strategies to synthesize these species are based (i) on the use of dissymmetric polynucleating ligands,[3] (ii) on the use of both the kinetic and thermodynamic stability "self-assembly method",[4] or (iii) on working step by step by using "complexes as ligands".[5] A nice example of this latter case is represented by the (oxamidato)copper(II) complexes.[6] Although

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